

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Applicants: T. UCHIDA, et al.

Application No.: 09/763,891

Filed: June 11, 2001

For: POLISHING SOLUTION FOR METAL AND POLISHING METHOD

Art Group: 1765

Examiner: Lynette T. Umez Eronini

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DECLARATION UNDER 37 CFR § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Yasuo KAMIGATA, a citizen of Japan, residing at 5-28, Kasuga 1-chome, Tsukuba-shi, Ibaraki-ken 305-0821, Japan, DECLARE THAT:

1. I earned a Bachelor of Science degree from Tokyo Metropolitan University in 1983, with a specialty in applied chemistry; and I earned a Masters of Science degree from Tokyo Metropolitan University in 1985, also with a specialty in applied chemistry.

2. I joined Hitachi Chemical Company, Ltd. in 1985, and have been employed by Hitachi Chemical Company, Ltd. since 1985.

(a) From 1985-1992 I worked on the development of thin film electroluminescent displays;

(b) From 1992-1995 I worked on the development of secondary battery materials;

(c) From 1995-1998 I worked on the development of color filters for LCD displays; and

(d) From 1998 to the present I have been working on the development of Chemical Mechanical Planarization slurries.

3. I am one of the named inventors in Application No. 09/763,891, given a filing date of June 11, 2001, for POLISHING SOLUTION FOR METAL AND POLISHING METHOD.

4. I note the statement by the Examiner in lines 5-8 of Item 8 on page 4 of the Office Action mailed May 7, 2003, in Application No. 09/763,891, that U.S. Patent No. 5,770,095 to Sasaki, et al. teaches a polishing solution which contains, among other components -

“an amino acetic acid (such as glycine, column 4, line 2) and/or an amidosulfuric acid (column 4, lines 50-52) which is the same as applicant's oxidized-metal dissolving agent and second protective film forming agent”

5. Contrary to this statement by the Examiner, glycine and/or an amidosulfuric acid do not qualify as a second protective-film forming agent as in the present invention. For showing that glycine and/or amidosulfuric acid do not qualify as the second protective-film forming agent as in the present invention, and in order to establish differences between the polishing solution for metal and method of use thereof, described and claimed in Application No. 09/763,891, on the one hand, and the polishing solution and method of use thereof described in U.S. Patent No. 5,770,095 to Sasaki, et al., on the other hand, the following experiments were conducted.

6. Polishing rate and etching rate of the following four solutions were investigated (listed amounts are parts by weight):

(a) Solution (1)

<u>Component</u>	<u>Amount</u>
Glycine	0.15
Water	70
Benzotriazole	0.2
Methanol	0.8
Amidosulfuric Acid	0.05
Hydrogen Peroxide (30%)	33.2

(b) Solution (2)

<u>Component</u>	<u>Amount</u>
Amidosulfuric Acid	0.15
Water	70
Benzotriazole	0.2
Methanol	0.8
Glycine	0.05
Hydrogen Peroxide (30%)	33.2

(c) Solution (3)

<u>Component</u>	<u>Amount</u>
Glycine	0.15
Water	70
Benzotriazole	0.2
Methanol	0.8
Glycine	0.05
Hydrogen Peroxide (30%)	33.2

(d) Solution (4)

<u>Component</u>	<u>Amount</u>
Amidosulfuric Acid	0.15
Water	70
Benzotriazole	0.2
Methanol	0.8
Amidosulfuric Acid	0.05
Hydrogen Peroxide (30%)	33.2

In the solutions (1)-(4), the methanol was a solvent for the benzotriazole. The glycine and amidosulfuric acid have been incorporated in solutions (1)-(4) in light of the above-quoted statement by the Examiner set forth in Item 4 herein, that U.S. Patent

No. 5,770,095 discloses a polishing solution containing an amino acetic acid (such as glycine) and/or an amidosulfuric acid which is the same as Applicants' oxidized-metal dissolving agent and second protective-film forming agent.

7. Polishing was conducted under the following processing conditions:

(a) That is, an electroplated copper film formed in a thickness of $1\ \mu\text{m}$ on a silicon substrate having a diameter of 12.5 cm was subjected to polishing using a respective solution (1), (2), (3) and (4) described above.

(b) Polishing was performed on the silicon substrate having the electroplated copper film, using a polishing pad IC1000 available from Rodel Co., the polishing pad being a single layer having an x-y groove. The polishing pressure was $210\ \text{g/cm}^2$, and the substrate/polishing platen relative speed (speed at the center of the substrate) was 36 m/min. The platen speed was 60 rpm, and the radius between the center of the polishing pad and the center of the substrate was 9.5 cm. Flow rate of the solutions (1), (2), (3) and (4) was 50 ml/min. Time of polishing was 1 minute.

8. A difference in layer thickness of the copper film before and after polishing was calculated from the value of electrical resistance of the copper film, using a measuring tool of electrical resistance, and the difference in layer thickness found was divided by treatment time to determined the polishing rate.

9. Etching was conducted under the following processing conditions, which are processing conditions, set forth in connection with Examples 1-12 and Comparative Examples 1-5, described on page 30 of Application No. 09/763,891:

(a) That is, a same electroplated substrate as was used in the polishing described in Item 7 above was separately prepared.

(b) A 2cm x 2cm square-diced chip of the substrate was immersed in a respective solution (1), (2), (3) and (4) as described above, with the respective solution being stirred at a stirring speed of 100 rpm. The stirring was performed by rotating the square-diced chip at 100 rpm, the substrate being rotated with an axis of rotation perpendicular to a surface of the 2cm x 2cm square-diced chip of the substrate having the Cu film thereon, at the center thereof. Temperature of the solution during immersion was 25°C, and treatment time was 10 minutes.

10. A difference in layer thickness of the copper film before and after etching was calculated from the value of electrical resistance of the copper film, using the same measuring tool of electrical resistance used in calculating the difference in layer thickness before and after polishing as discussed in Item 8 above; and the difference in layer thickness was divided by treatment time to determine the etching rate.

11. The following etching and polishing rates were found for solutions (1), (2), (3) and (4):

Solution	Polishing Rate (nm/min)	Etching Rate (nm/min)
(1)	8.7	0.39
(2)	72	6.8
(3)	3.8	0.03
(4)	98	24

12. From the results shown in Item 11, solutions (2) and (4) had unsatisfactorily large etching rates with respective polishing rates of 72 nm/min and 98 nm/min, and solutions (1) and (3) had unsatisfactorily low polishing rates.

13. For comparison purposes, note Example 7 set forth in Table 1 on page 32 of Application No. 09/763,891. Polishing processing was performed using the solution

of this Example 7, on a substrate as set forth in Item 7(a) herein (that is, the substrate had an electroplated copper film formed in a thickness of 1 μ m on a silicon substrate having a diameter of 12.5 cm), under processing conditions set forth in Item 7(b) herein. Etching processing was performed using the solution of this Example 7, on a substrate as set forth in Item 9(b) herein (that is, a 2cm x 2cm square-diced chip of the substrate having the Cu film thereon), under processing conditions set forth in Item 9(b) herein. In performing this polishing processing and etching processing using the solution of Example 7, the solution of Example 7 had a polishing rate of 185 nm/min and an etching rate of 0.2 nm/min.

14. From a comparison of the results in Items 12 and 13 in the foregoing, an unexpectedly greater polishing rate and unexpectedly lower etching rate is achieved for the solution of Example 7 of Application No. 09/763,891, having the second protective-film forming agent and being within the scope of the presently claimed invention, as compared with solutions (1), (2), (3) and (4) set forth in Item 6 in the foregoing.

15. As can be seen in comparing the results in Item 12 with the results in Item 13, the present invention having both the first and second protective film-forming agents with the oxidizing agent, oxidized-metal dissolving agent and water, achieves a desired unexpectedly higher polishing rate with unexpectedly lower etching rate (that is, unexpectedly better polishing rate with decreased etching rate), as compared with solutions, which the Examiner contends are disclosed in U.S. Patent No. 5,770,095, containing an oxidizing agent, benzotriazole, water, and an amino acetic acid (such as glycine) and/or amidosulfuric acid.

16. A comparison of the result in Items 12 and 13 shows that solutions (1)-(4), which do not contain a second protective-film forming agent as in the present invention,

do not achieve unexpectedly high polishing rate and reduced etching rate achieved by the present invention.

The undersigned hereby declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine, or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Yasuo KAMIGATA